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Ovshinsky et al.

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[54] **METHOD OF PREPARING A MAGNETIC MATERIAL**

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[51] **Int. Cl.**⁴ **C22C 1/04**
[52] **U.S. Cl.** .... **75/0.5 AA**; 75/0.5 AB
[58] **Field of Search** .... 75/0.5 AA, 0.5 AB

[56] **References Cited**

U.S. PATENT DOCUMENTS

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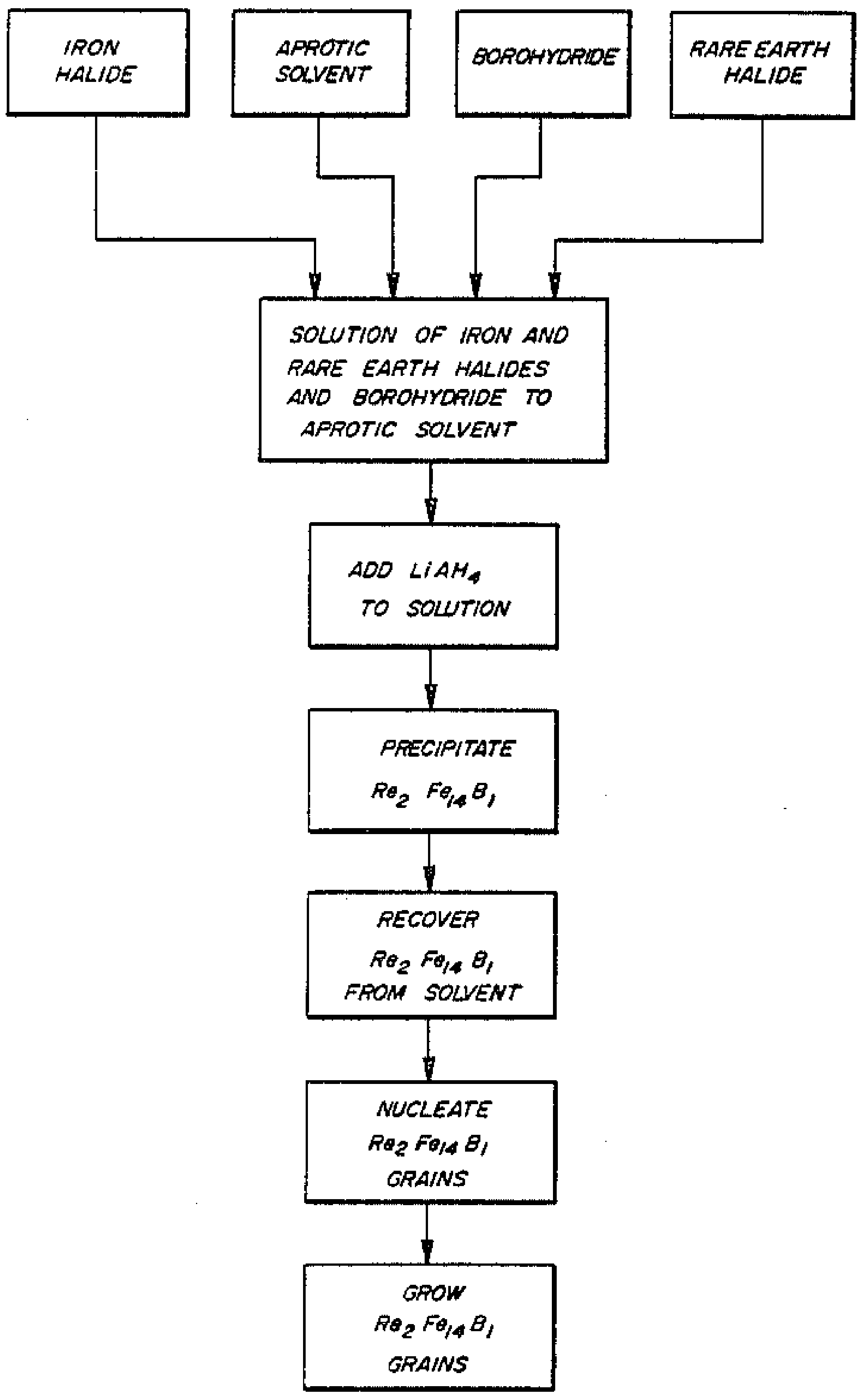
[57] **ABSTRACT**

A method of forming a magnetic material. The magnetic material is a solid mass of grains, and has magnetic parameters characterized by: (1) a maximum magnetic energy product, $(BH)_{max}$, greater than 15 megagausso-ersteds; and (2) a remanence greater than 8 kilogauss. The magnetic material is prepared by a two step solidification, heat treatment process. The solidification process is carried out by: (a) forming a solution of reducible precursor compounds of the magnetic material; and (b) thereafter reducing the reducible, precursor compounds and forming a precipitate thereof. The precipitate has a morphology characterized as being one or more of (i) amorphous, (ii) microcrystalline, or (iii) polycrystalline. The grains within the precipitate have, at this stage of the process, an average grain characteristic dimension less than that of the heat treated magnetic material. In the second, or heat treating, stage of the process, the precipitated solid is heat treated to form a solid material comprised of grains meeting at grain boundaries. The grains and grain boundaries have the morphology of the magnetic material.

13 Claims, 1 Drawing Figure



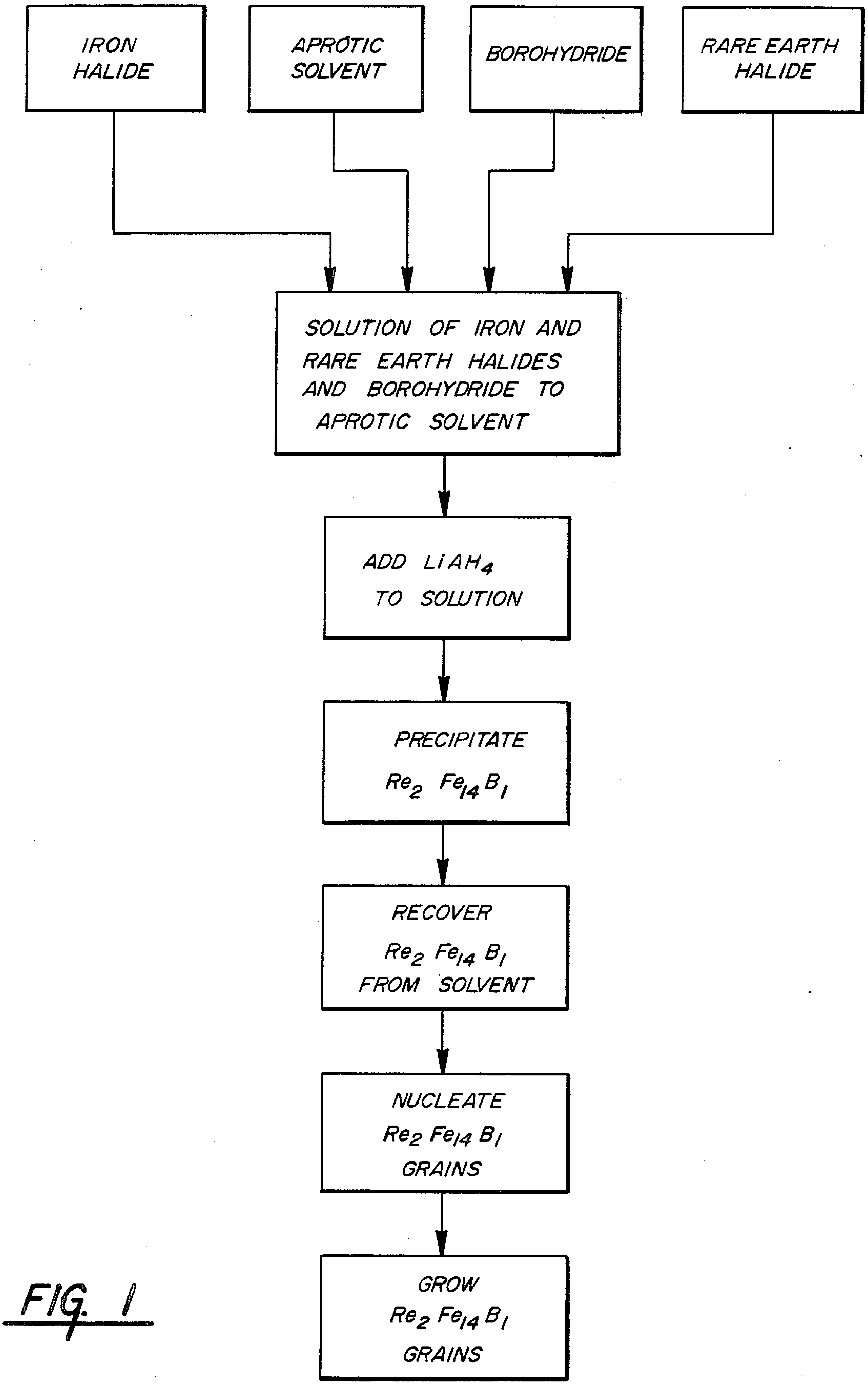

IRON HALIDE
APROTIC SOLVENT
BOROHYDRIDE
RARE EARTH HALIDE
SOLUTION OF IRON AND RARE EARTH HALIDES AND BOROHYDRIDE TO APROTIC SOLVENT
ADD LiAH4 TO SOLUTION
PRECIPITATE Re2 Fe14 B1
RECOVER Re2 Fe14 B1 FROM SOLVENT
NUCLEATE Re2 Fe14 B1 GRAINS
GROW Re2 Fe14 B1 GRAINS

FIG. 1

METHOD OF PREPARING A MAGNETIC MATERIAL

FIELD OF THE INVENTION

The invention relates to permanent magnetic alloy materials and methods of preparing them.

BACKGROUND OF THE INVENTION

There has long been a need for a relatively inexpensive, strong, high performance, permanent magnet. Such high performance permanent magnets would be characterized by relatively high magnetic parameters, e.g. coercive force (H_c) or coercivity, remanent magnetization or remanence, and maximum energy product.

Moreover, an ideal high-performance permanent magnet should exhibit a square magnetic hysteresis loop. That is, upon application of an applied magnetic field H greater than the coercive force Hc, all of the microscopic magnetic moments should align parallel to the direction of the applied force to achieve the saturation magnetization Ms. Moreover, this alignment must be retained not only for $H=0$ (the remanent magnetization Mr), but also for a reverse applied magnetic force of magnitude less than Hc. This would correspond to a maximum magnetic energy product (the maximum negative value of BH) of

$$(Mr^2/4)=(Ms^2/4)$$

Unfortunately, this ideal situation is at best metastable with respect to the formation of magnetic domains in other directions, which act to reduce Mr and BH_{max}.

Conventional high-performance permanent magnets that approach square-loop behavior have four general requirements:

1. The material must be composed primarily of a ferromagnetic element or compound with a Curie temperature Tc that significantly exceeds the application temperature Ta, and with Ms at Ta large. Practically speaking, this requires either Fe or Co as the major constituent.
2. In order to obtain a high coercive force, the material must consist of an assembly of small particles or crystallites.
3. These particles or crystallites must exhibit microscopic magnetic anisotropy, i.e. they must have a preferred "easy axis" of magnetization. This can follow either from shape anisotropy or magneto-crystalline interaction.
4. These microscopically anisotropic particles must be aligned substantially in parallel within the macroscopic assembly, in order to achieve values of Mr that approach Ms, i.e. square-loop behavior.

The prior art teaches that good permanent magnetic materials, e.g., having maximum magnetic energy products of about 15 megagaussoersteds, consist of a conglomeration of non-interacting substantially crystallographically oriented uniaxial particles. When a sufficiently large magnetic field is applied in a given direction, the individual vector magnetizations of each of these particles point along the applied field, corresponding to the maximum or saturation value of the net magnetization, M_s. As the applied magnetic field is reduced to zero, the vector magnetization of each particle relaxes back to the easy magnetic axis of the particle, so that the net resultant remanent magnetization, M_r, may be less than M_s.

This is more fully elucidated by the following geometrical model, in which the "easy axis" of magnetization lies along a preferred axis, c. For an isolated uniformly magnetized particle, the magnetization vector, M, lies along the c axis for a zero applied field. If a field is applied in an arbitrary direction z, the magnetization is rotated away from the c axis until, at sufficiently large fields, M is parallel to z and M_z is equal to M_s. When the field is removed, the magnetization relaxes back parallel to the c axis, subject to the condition that the projection of magnetization along the c axis is positive.

E. C. Stoner and E. V. Wohlfarth, Phil. Trans. Royal Soc. (London), A. 240, 599 (1948) have calculated the hysteresis loop for such a particle for different orientations of the c axis with respect to z. For the case of a sample comprising a large number of such non-interacting particles oriented along some direction, the magnetic properties for the material or sample are the sum or average of the properties of the individual particles. Such a sample or material is hereinafter referred to as an anisotropic material. Anisotropic materials have at least one magnetic property which is a strong function of the direction of measurement. Such materials are characterized by a single "easy direction" of magnetization, where the value of the property greatly exceeds the value in other directions of magnetization. If the particles are non-interacting, the maximum energy product varies from a maximum value of $0.25\ (M_s)^2$, when z is parallel to the c axis, to 0 when z is perpendicular to the c axis. For a theoretical anisotropic material with M_s equal to 16 and H_c chosen to be greater than M_s, the maximum theoretical value of the energy product of the hysteresis loop is 64 megagaussoersteds.

Stoner and Wohlfarth have carried out the same method of analysis for an ideal array of randomly oriented non-interacting uniformly magnetized particles. Since the array is isotropic there is no dependence of the hysteresis loop on the direction of the applied field. The maximum theoretical value of the energy product of such a loop is dependent on M_s and H_c. If M_s is chosen to equal 16 kilogauss and H_c is chosen to be much greater than M_s, then the maximum energy product is 16 megagaussoersteds.

Hence, the teaching of the prior art for a perfectly oriented non-interacting material (anisotropic) is that the maximum energy product is at least four (4) times that of the same material when randomly oriented (isotropic).

For a general distribution of orientations of non-interacting particles, as a consequence of simple vector geometry,

$$(M_r/M_s)=[\cos(\text{theta})],$$

where theta is the angle between the applied field and the easy axis of a given particle, and the result, indicated by double brackets, represents the size weighted average over all of the particles. As is well understood in the art, $M_r/M_s=1$ along the direction of orientation of a perfectly oriented, non-interacting, permanent magnet sample (anisotropic), and $M_r/M_s=0.5$ in all directions for a completely unoriented, non-interacting sample (isotropic). See, e.g., R. A. McCurrie, "Determination of the Easy Axis Alignment in Uniaxial Permanent Magnets for Remanence Measurements", J. Appl. Phys., Vol. 52, (No. 12), pages 7344–7346 (December

1981). Observations in the literature are consistent with this prediction. See, e.g., J. F. Herbst and J. C. Tracy, "On Estimating Remanent Magnetization from X-Ray Pole Figure Date", J. Appl. Phys., Vol. 50 (No. 6), pp. 4283–4284 (June 1979).

A figure of merit, which applicants refer to as the magnetic retention parameter, is

$$Q=Sum_{x,y,z}(M_rM_S)^2,$$

where M_s and M_r are measured with the applied magnetic field along three orthogonal directions. Theoretically, for magnetic materials of the prior art, Q approaches 1 for perfectly oriented, non-interacting, particles or crystallites (anisotropic) and 0.75 for completely unoriented, non-interacting, crystallites (isotropic). The behavior for reported values of permanent magnetic materials of the prior art tend to produce values of Q which are substantially below the theoretical values. See, e.g., McCurrie; Herbst and Tracy; and Stoner and Wohlfarth; above.

Prior art systems which are non-interacting and conform to the assumptions of and models in Stoner and Wohlfarth are described in the Background sections of commonly assigned copending U.S. application Ser. No. 816,778, filed Jan. 10, 1986, of R. Bergeron, R. McCallum, K. Canavan, and J. Keem for *Enhanced Remanence Permanent Magnetic Alloy Bodies and Methods of Preparing Same,* and U.S. application Ser. No. 893,516, filed Aug. 5, 1986 of R. Bergeron, R. McCallum, K. Canavan, J. Keem, A. Kadin, and G. Clemente, for *Enhanced Remanence Permanent Magnetic Alloy and Bodies Thereof.* The prior art materials described and discussed in the Background sections of our earlier applications do not exhibit any deviations from the assumptions and models of Stoner and Wohlfarth.

Deviations from (M_rM_s) =[Cos(theta)]corresponding to larger values of Mr might be expected to occur if the particles were permitted to interact with one another. Suggestions of this sort have appeared in the magnetic recording literature, where the proposed interaction was due to long range magnetic dipole fields. See, for example, H. N. Bertram and A. K. Bhatia, *The Effect of Interaction on the Saturation Remanence of Particulate Assemblies,* IEEE Trans. on Magnetics, MAG-9, pp 127–133 (1983), and R. F. Soohoo, *Influence of Particle Interaction on Coercivity and Squareness of Thin Film Recording Media,* J. Appl. Phys., Vol 52(3), pp 2459–2461 (1981). However, this assumption of interactions has been questioned. See, for example, P. M. Davis, *Effects of Interaction Fields on the Hysteretic Properties of Assemblies of Randomly Oriented Magnetic or Electric Moments,* J. Appl. Phys., Vol 51 (2), pp 594–600 (1980).

Suggestions of short range interactions based on exchange have also been made with respect to amorphous iron-rare earth alloys at cryogenic temperatures by E. Callen, Y. L. Liu, and J. R. Cullen, *Initial Magnetization, Remanence, and Coercivity of the Random Anisotropy Amorphous Ferromagnet* Phys. Rev. B, Vol. 16, pp 263–270 (1977).

The literature does not contain any verified indications of enhanced values of Mr relative to those predicted by Stoner and Wohlfarth, above, in isotropic permanent magnetic materials.

However, contrary to the limited but negative teachings of the prior art interaction between crystallites has been used to achieve enhanced magnetic properties in bulk solid materials. Magnetic materials which utilize interaction are described in commonly assigned copending U.S. application Ser. No. 816,778, filed Jan. 10, 1986, of R. Bergeron, R. McCallum, K. Canavan, and J. Keem for *Enhanced Remanence Permanent Magnetic Alloy Bodies and Methods of Preparing Same,* and U.S. application Ser. No. 893,516, filed Aug. 5, 1986 of R. Bergeron, R. McCallum, K. Canavan, J. Keem, A. Kadin, and G. Clemente, for *Enhanced Remanence Permanent Magnetic Alloy and Bodies Thereof,* both of which are incorporated herein by reference.

Described therein is a class of permanent magnetic alloys which exhibit superior magnetic properties as measured in all spatial directions, that is, isotropically. The magnetic parameters are of a magnitude which the prior art teaches to be only attainable in one spatial direction, that is, anisotropically, and to be only attainable with aligned materials.

The magnetic materials described in the incorporated patent applications have a ratio of net remanent magnetization (M_r) to net saturation magnetization (M_s), exceeding 0.5 and approaching 1.0, in all directions, without any significant preferred crystallite orientation. This is a clea violation of the consequences of the Stoner and Wohlfarth's model and the assumptions of the prior art that the grains must be microscopically anisotropic grains that are aligned substantially in parallel within the macroscopic body in order to achieve values of Mr approaching Ms, i.e., square hysteresis loop behavior.

These permanent magnetic materials have isotropic magnetic retention parameters, Q, as described above, greater than 0.75 and preferably greater than 1. The theoretical limit of the magnetic retention parameter, Q, for the herein contemplated materials is believed to approach 3, rather than the theoretical values of 1.0 and 0.75 respectively, for aligned (anisotropic) and unaligned (isotropic), non-interacting materials of the prior art.

Ribbon samples of the as quenched materials described above, without further processing, exhibit remanent magnetization, M_r, greater than 8 kilogauss, coercive force, H_c, greater than 8 kilooersteds, and preferably greater than 11 kilooersteds, and maximum energy product (BH)max greater than 15 megagaussoersteds with similar values measured in all directions, i.e., in the plane of the ribbon and perpendicular to the plane of the ribbon. In the latter case the value was obtained after a standard correction (a geometric demagnetization factor as described, for example, in R. M. Bozorth, *Ferromagnetism,* D. VanNostrand Co., New York, (1951), at pages 845–847) for the shape anisotropy of the ribbon.

The saturation magnetization M_s of the ribbon, i.e., the magnetization in the limit for large applied fields, e.g., an applied magnetic field above about 50 kilogauss, is 15 to 16 kilogauss, also in all directions. In order to directly measure saturation magnetization, M_s, the applied field should be at least three times the coercive force, H_c. Alternatively, the value of M_s can be estimated based on the values thereof for compositionally similar materials. The values correspond to a value of M_r/M_s greater than 0.5, and a magnetic retention parameter, Q, greater than 0.75, in contradistinction to the clear teachings of the prior art for a macroscopically isotropic, non-interacting material.

Typical magnetic parameters for the magnetic alloys described in the above incorporated patent application are as shown in Table I of U.S. application Ser. No. 893,516, filed Aug. 5, 1986, Table V of U.S. patent application Ser. No. 816,778. (An M_s of 16 kilogauss was used.)

As can be seen from Table I of U.S. application Ser. No. 893,516, filed Aug. 5, 1986, the samples of the materials described therein exhibit superior relevant magnetic parameters throughout the volume of the bulk solid, evidencing interaction between grains. The properties are especially superior when compared with the properties of the isotropic materials of the prior art listed in Table III of U.S. application Ser. No. 816,778. When compared with the anisotropic prior art materials listed in Table IV of U.S. application Ser. No. 816,778, the samples of the inventions described in the aforementioned U.S. patent application Ser. Nos. 816,778 and 893,516 (filed Aug. 5, 1986) exhibit comparable but isotropic magnetic properties, and were prepared without the costly, complicated alignment steps necessary in the prior art.

The magnetic alloy materials of U.S. application Ser. Nos. 816,778 and 893,516 (filed Aug. 5, 1986) have been prepared by the melt spinning process, and more particularly by the free jet casting process.

In the free jet casting process a jet of molten metal is expelled under a head of inert gas from a crucible onto a rapidly rotating chill wheel. This jet of molten metal forms a puddle of molten metal on a rapidly rotating chill wheel. The top of the puddle appears to stand stationary beneath the orifice of the crucible, while the bottom of the puddle appears to be continuously drawn away from the crucible orifice. We have observed an instability associated with the interaction between the chill wheel and the puddle. This instability is associated with a high degree of variance of magnetic properties of the cast products and a concommitant low yield of enhanced remanence magnetic alloy material.

SUMMARY OF THE INVENTION

These instabilities of the free jet casting process and the associated low yields of enhanced remanence magnetic material are obviated by the method of this invention.

The magnetic material is prepared by a two step solidification, heat treatment process. The solidification process yields a very low coercivity material, characterized as being one or more of amorphous, microcrystalline, or polycrystalline. The grains within the solid have, at this stage of the process, an average grain characteristic dimension less than that of the heat treated magnetic material, and too small to provide a practical coercivity or an enhanced remanence.

The solidification process is carried out by forming a solution of reducible precursor compounds of the magnetic material in a suitable solvent. A suitable reductant or reducing agent is used to reduce the reducible, precursor compounds and form a precipitate thereof. Typically the solvent is an aprotic organic solvent and the reducing agent is a strong reductant, e.g., lithium aluminum hydride.

In the second, or heat treating, stage of the process, the atomized solid particles are heat treated to form a solid material having a morphology that provides a practical coercivity and the above described enhancement of remanence. The heat treated solid is comprised of grains meeting at grain boundaries, with the substantial absence of intergranular phases of different stoichiometry or structure. The grains and grain boundaries have the morphology of the enhanced remanence magnetic material.

THE FIGURES

The invention may be understood by reference to the following FIGURE. FIG. **1** is a flow chart of one method of carrying out the invention.

DETAILED DESCRIPTION OF THE INVENTION

According to the invention there is provided a method of forming a class of magnetic alloy materials having superior magnetic properties. These magnetic alloy materials are high remanence materials that do not obey the Stoner and Wohlfarth assumptions of non-interacting particles. To the contrary, the individual grains or crystallites interact across grain boundaries. The enhanced magnetic properties give clear evidence of this interaction across grain boundaries of the grian or crystallites.

The alloy is a substantially crystallographically unoriented, substantially magnetically isotropic alloy, with interaction between adjacent crystallites. By substantially isotropic is meant a material having properties that are similar in all directions. Quantitatively, substantially isotropic materials include those materials where the remanence along all three orthogonal axis, after application of the appropriate geometric demagnetization factor, are interactively enhanced, i.e., greater than 8 kilogauss, as well as those materials where the average value of [Cos(theta)], defined above, is less than about 0.75 in all directions, where Cos (theta) is averaged over all the crystallites. Microscopically this means that the direction of the easy axis of magnetization is substantially random and substantially uncorrelated from grain to grain.

The materials are permanent (hard) magnets, with isotropic magnetic parameters, i.e. isotropic maximum magnetic energy products greater than 15 megagaussoersteds, magnetic retention parameters, Q, greater than 0.75, standard temperature coercivities greater than about 8 kilooersteds, and remanences greater than about 8 kilogauss, and preferably greater than above about 11 kilogauss.

The saturation magnetization M_s of the ribbon, i.e., the magnetization in the limit of large applied fields, is 15 to 16 kilogauss, also in all directions. These values correspond to a value of M_r/M_s greater than 0.5, and a magnetic retention parameter, Q, greater than 0.75, in contradistinction to the clear teachings of the prior art for a macroscopically isotropic material.

The magnetic material is composed of an assembly of small crystalline ferromagnetic grains.

The grains are in intimate structural and metallic contact along their surfaces, i.e., along their grain boundaries. They are characterized by the substantial absence of intergranular material of different stoichiometry or morphology. That is, one grain of the material is in direct contact with an adjacent grain of the material at a grain boundary that is substantially free of intergranular materials and/or phases. This is contradistinction of the clear teachings of Raja K. Mishra, "Microstructure of Melt-Spun Nd-Fe-B Magnequench Magnets," Journal of Magnetism and Magnetic Materials, Vol 54–57 (1986), pages 450–456 who teaches the necessity of a 10–20 Angstrom thick film of Nd-rich, B-lean phase, between $Nd_2Fe_{14}B_1$ grains. Mishra reports that this film is necessary as a pinning site for magnetic domain walls. By way of contrast, according to the instant invention grains of magneticmaterial are in direct contact with adjacent grains of magentic material, e.g., grains o $Nd_2Fe_{14}B$.

The degree of magnetic enhancement is determined by the average characteristic dimension of the grains, Ro, the size distribution of the individual grain dimensions relative to this characteristic scale, and a characteristic dimension of the grain boundaries. The characteristic dimension of the grain boundaries must be small enough to allow interaction between adjacent grains across the grain boundaries.

The magnetic alloys are solidified or quenched to produce a precursor microstructure, which, when appropriately heat treated, results in a structure having these dimensions and morphologies and therefore exhibiting the above described improved magnetic parameters. These initially solidified particles much larger then the characteristic grain dimension R_o. A particle may contain at least 10^8 grains of characteristic grain size R_o.

The as heat treated dimensions and morphologies are critical in obtaining the enhanced remanence and magnetic retention parameters herein contemplated.

While the illustrations of the interaction across grain boundaries in Ser. No. 893,516 have been quantitatively described with respect to rare earth-transition metal-boron materials of tetragonal, $P4_2/mnm$ crystallography, especially the $Nd_2Fe_{14}B_1$ type materials, this is a general phenomenon applicable to other systems as well. The optimum characteristic grain dimension R_o, however, may be different in these other cases.

We expect that for $Pr_{2-x}Nd_xFe_{14}B_1$, R_o will be approximately 200 Angstroms for all values of x. For $SmCo_5$, for example, where Curie temperature, Tc=900K, saturation magnetization, Ms=12 kG, and Hanisotropy=300 kOe, H(spin,spin)=9 MOe, so that R_o=(9 MOe)/(300 kOe)×2.5 Angstroms=(approximately) 80 Angstroms. Similarly, for Sm_2Co_{17} R_o=(12 MOe)/(8 OkOe)2.5 Angstroms=(approximately) 400 Angstroms.

For randomly-oriented crystallites at the optimum size, the expected magnetic enhancement attributable to quantum mechanical magnetic coupling is comparable to that estimated above for $Nd_2Fe_{14}B$ type material—an increase in BH_{max} by a factor of 2 to 3 above that predicted by the Stoner and Wohlfarth model, above.

The magnetic material is prepared by a two step precipitation, heat treatment process. The precipitation process yields a very low coercivity material, characterized as being one or more of amorphous, microcrystalline, or polycrystalline. The crystallites within the solid have, at this stage of the process, an average grain characteristic dimension less than that of the heat treated magnetic material, and too small to provide a practical coercivity.

The solidification process is carried out by forming a solution of reducible precursor compounds of the magnetic material in a suitable solvent. A suitable reductant or reducing agent is used to reduce the reducible, precursor compounds and form a precipitate thereof.

According to one embodiment of the invention reducible compounds of the elements of the magnetic alloy are introduced into a non-aqueous solvent, for example an aprotic solvent, and reduced with a strong reducing agent. The strong reducing agent is necessitated by the electronegativity of the rare earth metal. The strong reducing agents decompose water, necessitating an aprotic solvent.

By a strong reducing agent is meant a reducing agent more electronegative then the rare earth component of the alloy. For example, neodymium has an ionization potential

$$Nd = Nd^{+3} + 3e^-,\ E = -2.246\ V,$$

of 2.246 volts. Suitable reducing agents include, for example, $LiAlH_4$, or a dispersed (colliodal) alkali metal as Li, Na, K, Rh, or Cs (and especially Li, Na, and K).

These strong reducing agents readily decompose water, yielding gaseous hydrogen. Thus, it is necessary to carry out the reduction in an aprotic solvent. Aprotic solvents are those solvents, typically hydrocarbons and derivatives thereof. Aprotic solvents have minimal tendency to either gain or lose protons. They are essentially inert, exhibiting essentially no levelling effect. Aprotic solvents are further characterized by low dielectric constants, e.g., less than 6, and generally from 2 to 6. Exemplary aprotic solvents include ethers, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), tetrahydrofuran (THF), trimethylamine (TMA), triethylamine (TEA). trialkylamines, and the like.

According to a preferred exemplification which may have the flow chart shown in FIG. 1, simple salts of the rare earth metal, the iron, and boron are introduced into an aprotic organic solvent, and the solvent is reduced with a strong reducing agent. For example, simple halides, e.g., chlorides, bromides, iodides of (1) one or more of neodymium and praseodymium, and (2) iron, optionally with cobalt, are solublized with a simple borohydride, in an aprotic organic solvent.

The salts are reduced to metal with a strong reductant, as lithium aluminum hydride, or a dispersed (colloidal) alkali metal. Reduction may be carried out in a quiescent solution, or it may be carried out in a continuously mixed solution, as a continuously totally refluxed solution.

The metals may be precipitated directly upon reduction, thermally, by solvent extraction, change in pH, or further reaction. The precipitate may then be recovered by physical separation, as filtration, settling, sedimentation, centrifugation. Alternatively, the remaining lithium aluminum hydride, if any, may be neutralized, hydrolyzed, or decomposed, and the reduced materials thereafter precipitated, for example by the addition of a further solvent and/or a subsequent reaction or shift in the pH.

In the second, or heat treating, stage of the process, the solid particles are heat treated to form a solid material having a morphology that provides a practical coercivity and the above described enhancement of remanence. The heat treated solid is comprised of grains meeting at grain boundaries. The grains and grain boundaries have the above described morphology associated with the enhanced remanence magnetic material.

In one exemplification the magnetic alloy material is an alloy of iron, optionally with other transition metals, as cobalt, a rare earth metal or metals, boron, and a modifier. In another exemplification the magnetic alloy material is an alloy of a ferromagnetic transition metal as iron or cobalt, with an lanthanide, as samarium, and a modifier.

A modifier is an alloying element or elements added to a magnetic material which serve to improve the isotropic magnetic properties of the resultant material, when compared with the unmodified material, by an appropriate processing technique. Exemplary modifiers are silicon, aluminum, and mixtures thereof. Alternative or additional modifiers may include lithium, hydrogen, fluorine, phosphorous, sulfur, germanium, and carbon. It is possible that the modifier acts as a grain refining agent, providing a suitable distribution of crystallite sizes and morphologies to enhance interactions.

The amount of modifier is at a level, in combination with the quench parameters, to give the above described isotropic magnetic parameters.

While the alloys referred to herein have modifiers, which are believed to control grain nucleation and growth, the crystallite size and size distribution may be obtained by proper choice and control of the solidification technique employed. For example, such solidification methods as gas atomization, metallization, chemical vapor deposition, and the like may be used as an alternative to rapid solidification from the melt even without the modifier. The modifier acts during solidification from the liquid state, or during grain nucleation and growth from the amorphous state, e.g., as a grain refining agent or a nucleating agent, to provide the distribution of crystallite size and morphology necessary for enhanced properties.

When modifiers are indicated as being present, it is to be understood that other methods of providing nucleation sites and/or obtaining uniform grain size may be used.

The magnetic alloy may be of the type [Rare Earth Metal(s)]-[Transition Metal(s)]-[Modifier(s)], for example

[Sm]-[Fe, Co]-[Si, Al].

Another interacting alloy may be of the type [Rare Earth Metal(s)]-[Transition Metal(s)]-Boron-[modifier(s)],

for example [Rare Earth Metal(s)]-[Fe,Co]-Boron-[modifier(s)], and [Rare Earth Metal(s)]-[Fe,Co,Mn]-Boron-[modifier(s)].

In one exemplification, the magnetic alloy material has the stoichiometry represented by:

$(Fe,Co,N)_a$ $(Nd,Pr)_bB_c(Al,Si)_d$, exemplified $Fe_a(Nd,Pr)_bB_c(Al, Si)_d$,

where a, b, c, and d represent the atomic percentages of the components iron, rare earth metal or metals, boron, and silicon, respectively, in the alloy, as determined by energy dispersive spectroscopy (EDS) and wave length dispersive spectroscopy (WDS) in a scanning electron microscope;

$a+b+c+d=100$;

a is from 75 to 85;

b is from 10 to 20, and especially from 11 to 13.5;

c is from 5 to 10;

and d is an effective amount, when combined with the particular solidification or solidification and heat treatment technique to provide a distribution of crystallite size and morphology capable of interaction enhancement of magnetic parameters, e.g., from traces to 5.0.

The rare earth metal is a lanthanide chosen from neodymium and praseodymium, optionally with other lanthanides (one or more La, Ce, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), Sc, Y, and mixtures thereof present. While various combinations of the rare earth metals may be used without departing from the concept of this invention, especially preferred rare earth metals are those that exhibit one or more of the following characteristics: (1) the number of f-shell electrons is neither 0 (as La), 7 (as Gd) or 14 (as Lu), (2) low molecular weight lanthanides, such as La, Ce, Pr, Nd, and Sm, (3) high magnetic moment lanthanides that couple ferromagnetically with iron, as Nd and Pr, or (4) relatively inexpensive lanthanides, as La, Ce, Pr, and Nd. Especially preferred are Nd and Pr. Various commercial and/or byproduct mischmetals may be used. Especially preferred mischmetals are those rich in Nd and/or Pr.

While the invention has been described with respect to certain preferred exemplifications and embodiments thereof, it is not intended to limit the scope of the invention thereby, but solely by the claims appended hereto.

We claim:

1. A method of forming a magnetic material of the transition metal-rare earth metal-boron type comprising a solid mass of grains, which method comprising the steps of:

(a) forming a solution of a reducible iron halide, a reducible rare earth halide, and lithium borohydride in an aprotic solvent;

(b) reducing the compounds and precipitating a tetragonal, $RE_2Tm_{14}B$-type composition having a morphology characterized by one or more of

  (i) amorphous;

  (ii) microcrystalline; and

  (iii) polycrystalline; wherein the grains thereof have an average grain characteristic dimension less than that of the optimal enhanced remanence magnetic material; and

(c) heat treating the precipitate to form a solid material characterized in that the grains meet adjacent grains at grain boundaries therebetween, the grains and grain boundaries therebetween being characterized by:

  (i) the grains having an average grain characteristic dimension;

  (ii) individual grains having an easy axis of the magnetization and an individual grain characteristic dimension within a distribution about the average grain characteristic dimension; and

  (iii) the grain boundaries having a characteristic dimension small enough to allow interaction between surface atoms of adjacent grains across the grain boundaries, thereby forming a permanent magnetic material such that the grain-grain interaction in the heat treated material substantially equals the magnetic anisotropy field of the individual grains;

the magnetic material being characterized by:

  (1) a maximum magnetic energy product, $(BH)_{max}$, greater than 15 megagaussoersteds; and

  (2) a remanence greater than 8 kilogauss.

2. The method of claim 1 wherein the aprotic solvent is chosen from the group consisting of TEA, TMA, THF, DMSO, and DMF.

3. The method of claim 1 wherein the interaction between adjacent grains of the heat treated magnetic material is strong enough to magnetically align the grain away from its easy axis of magnetization.

4. The method of claim 1 wherein the anisotropy energy of the individual grains of the heat treated magnetic material is strong enough to result in a coercivity about about 8 kilooersteds.

5. The method of claim 1 wherein the alloy has the nominal composition $RE_2TM_{14}B_1$, where RE represents a rare earth metal or metals, and TM represents a transition metal or metals.

6. The method of claim **5** wherein the rare earth metal is chosen from the group consisting of praseodymium and neodymium.

7. The method of claim **5** wherein the transition metal is chosen from the group consisting of iron, cobalt, and nickel.

8. The method of claim **5** wherein the magnetic material further comprises one or more modifiers.

9. The method of claim **8** wherein the modifier is chosen from the group consisting of aluminum and silicon.

10. The method of claim **8** wherein the modifier is a grain refining agent.

11. The method of claim **10** wherein the grain refining agent modulates the competing rates nucleation and grain growth to provide a solid, heat treated magnetic material with a characteristic grain dimension, R_o, of about 200 Angstroms, and a distribution about the characteristic dimension to substantially avoid the effects of low coercivity and multidomain grains.

12. The method of claim **5** wherein the heat treated magnetic material consists essentially of a tetragonal phase of $P4_2/mnm$ crystallography.

13. The method of claim **12** wherein the tetragonal phase has the nominal composition:

$$Fe_a(Nd,Pr)_bB_c(Si,Al)_d$$

where

$75 \leqq a \leqq 85$,

$10 \leqq b \leqq 20$,

$5 \leqq c \leqq 10$, and

$0 \leqq d \leqq 5$.

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